

# Thermal Superradiance and the Clausius-Mossotti Lorentz-Lorenz Equations

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**Abstract.** Electric polarization phenomena in insulating systems have long been described in mean field theory by the (static) Clausius-Mossotti or (dynamic) Lorentz-Lorenz polarizabilities. It is here shown, in the strong coupling regime, that a thermodynamic phase instability exists in these models. The resulting thermodynamic phase diagram coincides with that obtained from Dicke-Preparata model of thermal superradiance.

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A property of fundamental importance in the physics and chemistry of condensed matter insulators is the dielectric response function

$$\varepsilon = 1 + 4\pi\chi \quad (1)$$

In principle,  $\varepsilon$  is largely determined by the polarizability[1-12]  $\alpha$  of the constituent molecules. Precisely relating  $\varepsilon$  to  $\alpha$  is a statistical thermodynamic problem of considerable complexity. In the lowest order mean field theory approximation, the problem is solved by the Clausius-Mossotti equation[13-16]

$$\left(\frac{4\pi\alpha}{3v}\right) = \left(\frac{\varepsilon - 1}{\varepsilon + 2}\right), \quad (2)$$

where  $v$  is the volume per molecule. Equivalently, the mean field Clausius-Mossotti electric susceptibility is then

$$\chi = \left(\frac{(\alpha/v)}{1 - (4\pi\alpha/3v)}\right). \quad (3)$$

Note that the stability of Clausius-Mossotti mean field theory requires the inequality for the static polarizability

$$4\pi\alpha < 3v \quad (\text{stable normal phase}). \quad (4)$$

When the above inequality is violated, the normal phase becomes unstable and a new stable phase appears. Our purpose is to show that this new stable phase is nothing but the superradiant phase implicit in superradiant[17-26] Dicke-Preparata models. The

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derivation of the superradiant phase diagram is considerably simplified. To see what is involved, one may consider the response functions  $\alpha$ ,  $\chi$  and  $\varepsilon$  generalized to finite frequency  $\omega$ .

When the response functions are contemplated at finite frequency, for example in the index of refraction  $n(\omega) = \sqrt{\varepsilon(\omega)}$ , the Clausius-Mossotti Eqs.(1), (2) and (3) become the Lorentz-Lorenz equations[27-30]. These have a surprising feature regarding frequency shifts. For example, suppose that a single atom with atomic number  $Z$  has a strong resonance at frequency  $\omega_\infty$ , i.e. with  $m$  as the electron mass,

$$\alpha(\omega) \approx \left( \frac{Ze^2}{m} \right) \frac{1}{\omega_\infty^2 - \omega^2 - 2i\gamma\omega}, \quad (5)$$

Eqs.(3) and (5) then imply

$$\chi(\omega) \approx \left( \frac{Ze^2}{vm} \right) \frac{1}{\omega_0^2 - \omega^2 - 2i\gamma\omega}, \quad (6)$$

with a “renormalized” resonant frequency  $\omega_0$  given by

$$\omega_0^2 = \omega_\infty^2 - \left( \frac{4\pi Ze^2}{3vm} \right) = \omega_\infty^2 \left\{ 1 - \left( \frac{4\pi\alpha}{3v} \right) \right\}, \quad (7)$$

where  $\alpha \equiv \alpha(\omega = 0)$  is the static polarizability. The *macroscopic* Lamb frequency shift  $\Delta\omega = \omega_\infty - \omega_0$  is certainly worthy of note. It is due to the coherent collective oscillation of a large number of molecular dipole moments.

Electric dipolar motions in (say) a single atom move at a Bohr frequency  $\omega_\infty$  determined by the energy difference between two states  $|i\rangle$  and  $|f\rangle$  connected by a dipole matrix element  $\langle f | \mathbf{p} | i \rangle \neq 0$ , i.e.  $\hbar\omega_\infty = (\epsilon_f - \epsilon_i)$ . In a condensed matter sample of similar atoms, the dipolar motions in one atom radiate an electromagnetic field which can drive a neighboring atomic dipole into oscillation. The motion can become collective. In the *mean field* theory of Clausius-Mossotti and Lorentz-Lorenz, the driving collective macroscopic electric field  $\bar{\mathbf{E}}$  is related to the dipole moment per unit volume  $\mathbf{P}$  via  $\bar{\mathbf{E}} = -(4\pi/3)\mathbf{P}$ . The mean electric field phase locks the oscillations of many atoms. The collective motions of the large number of dipoles yields the macroscopic Lamb shift frequency renormalization  $\omega_\infty \rightarrow \omega_0$  in accordance with Eq.(7). Mean field  $\bar{\mathbf{E}}$  theory thereby implies a new collective Bohr frequency which from a quantum mechanical viewpoint arises from more closely spaced macroscopic energy levels  $\hbar\omega_0 = (E_f - E_i) < \hbar\omega_\infty = (\epsilon_f - \epsilon_i)$ .

At the critical temperature  $T_c$  for stability, we have from the static polarizability stability Eq.(4) the condition

$$\left( \frac{4\pi\alpha(T_c)}{3} \right) = v \quad (\text{critical point}), \quad (8)$$

where  $\alpha_c = \alpha(T_c)$ . From the dynamical Eq.(7) viewpoint, the renormalized frequency is lowered to zero at the critical temperature  $\lim_{T \rightarrow T_c+} \{\omega_0(T)\} = 0$  which again leads to Eq.(8).

In order to compute  $\alpha(T)$  one needs a model Hamiltonian  $H_{mol}$  for a single molecule. In the presence of an external electric field  $\mathbf{F}$  one may then compute the single molecule partition function

$$\Phi(\mathbf{F}, T) = -k_B T \ln \left( \text{Tr} e^{-(H_{mol} - \mathbf{p} \cdot \mathbf{F})/k_B T} \right). \quad (9)$$

where  $\mathbf{p}$  is the electric dipole operator of the molecule. The mean dipole moment is determined by

$$d\Phi = -sdT - \bar{\mathbf{p}} \cdot d\mathbf{F}, \quad (10)$$

and the polarizability of the molecule is given by

$$\alpha_{ij} = \lim_{|\mathbf{F}| \rightarrow 0} \left( \frac{\partial \bar{p}_i}{\partial F_j} \right)_T. \quad (11)$$

For a “two level atom” corresponding to the Dicke model, one chooses the model Hamiltonian

$$H_2 - \mathbf{p}_2 \cdot \mathbf{F} = \begin{pmatrix} -\Delta & -\mu F \\ -\mu F & \Delta \end{pmatrix} \quad (12)$$

yielding

$$\Phi_2 = -k_B T \ln 2 - k_B T \ln \left\{ \cosh \left( \frac{\sqrt{\Delta^2 + \mu^2 F^2}}{k_B T} \right) \right\} \quad (13)$$

so that

$$\alpha_2(T) = \left( \frac{\mu^2}{\Delta} \right) \tanh \left( \frac{\Delta}{k_B T} \right). \quad (14)$$

Employing Eqs.(8) and (14) and the definition of the critical volume per two-state atom

$$v_c = \left( \frac{4\pi\mu^2}{3\Delta} \right) \quad (15)$$

we find for the critical temperature of the Clausius-Mossotti model for two state atoms

$$k_B T_{c2} = \left( \frac{2\Delta}{\ln \{ (v_c + v)/(v_c - v) \}} \right). \quad (16)$$

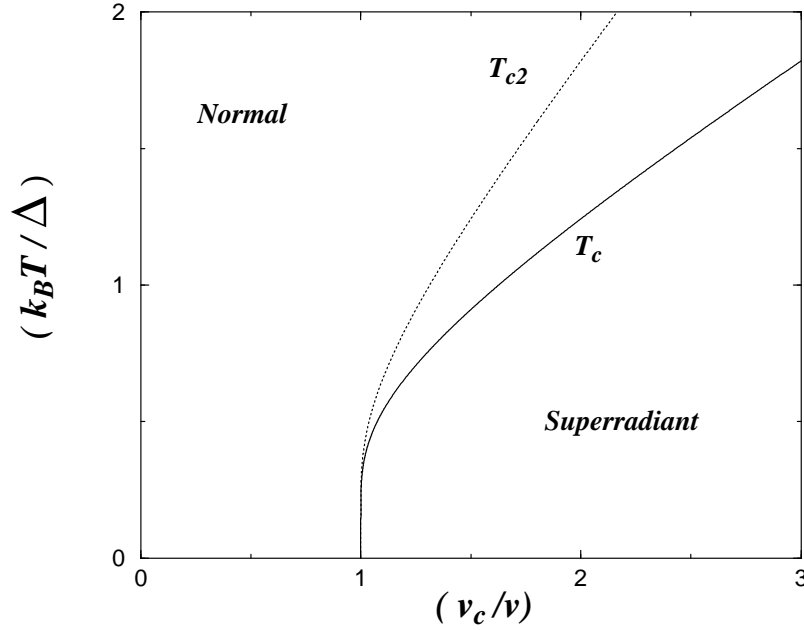
The above Eq.(16) is identical to the critical temperature of the Dicke model as derived in previous work[31, 32].

For atoms in an electronic zero angular momentum ( $J = 0$ ) state, it is more realistic to consider a four state model with three ( $J = 1$ ) degenerate states ( $M_J = 0, \pm 1$ ). The resulting Hamiltonian four state matrix may then be written as

$$H - \mathbf{p} \cdot \mathbf{F} = \begin{pmatrix} -\Delta & -\mu F_x & -\mu F_y & -\mu F_z \\ -\mu F_x & \Delta & 0 & 0 \\ -\mu F_y & 0 & \Delta & 0 \\ -\mu F_z & 0 & 0 & \Delta \end{pmatrix}. \quad (17)$$

The free energy implicit in the Hamiltonian matrix of Eq.(17) may be written as

$$\Phi = -k_B T \ln 2 - k_B T \ln \left\{ e^{-\Delta/k_B T} + \cosh \left( \frac{\sqrt{\Delta^2 + \mu^2 |\mathbf{F}|^2}}{k_B T} \right) \right\} \quad (18)$$



**Figure 1.** Shown as a “solid curve” is the critical temperature  $T_c$  for the four level atom as computed from Eq.(20). The curve divides the  $(T, v)$  plane into regions which are either superradiant or normal. The “dotted curve” shows the critical temperature which follows from the superradiant[31, 32] Dicke two level atom model.

so that

$$\alpha(T) = \left( \frac{\mu^2}{\Delta} \right) \frac{\sinh(\Delta/k_B T)}{\exp(-\Delta/k_B T) + \cosh(\Delta/k_B T)}. \quad (19)$$

Employing Eqs.(8), (15) and (19) yields the critical temperature  $T_c$  for the superradiant phase transition found by solving

$$\frac{\sinh(\Delta/k_B T_c)}{\exp(-\Delta/k_B T_c) + \cosh(\Delta/k_B T_c)} = \left( \frac{v}{v_c} \right). \quad (20)$$

The phase diagrams implicit in both Eqs.(16) and (20) are shown in Fig.1. The difference between the two level model and the four level model is merely a shift in the phase boundary. The existence of the superradiant phase is robust with respect to changes in the detailed model structure.

We have developed a very simple algorithm for finding the regions in the  $(T, v)$  plane for which the superradiant phase exists. Linear magnetic materials can be either paramagnetic or diamagnetic. Linear electrical systems can only occur in nature as paraelectrics. Diaelectric systems can be ruled out[33]. It is the absence of diaelectricity which accounts for the reliability of the algorithm. The computation of the phase diagram requires (i) a reliable computation of the single molecule polarizability, and (ii) the dielectric constant of the bulk material. The critical temperature has the form of

an implicit equation

$$\alpha(T_c) = g(v, T_c) \quad \text{where} \quad g_{CM} = \left( \frac{3v}{4\pi} \right). \quad (21)$$

The Clausius-Mossotti function  $g_{CM}$  is valid in mean field theory. The fluctuation corrections to Clausius-Mossotti mean field theory[34-39], (i.e. the precise  $g(v, T)$  function) may be computed systematically via perturbation theory. The corrections are merely quantitative. Qualitatively, the superradiant phase is shifted but left intact.

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